REPORT DOCUMENTATION PAGE

AD-A265 322

Form Approved OMB No 0704-0188

(2)

Public reporting burden for this collection of information is estim... gathering and maintaining the data needed, and completing and r... collection of information, including suggestions for reducing this b... Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the ... ructions, searching existing data sources ... rden estimate or any other aspect of this ... Operations and Reports, 1215 Jefferson ... 88), Washington DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 12, 1993	Technical Report # 13

4. TITLE AND SUBTITLE

New chromophores containing sulfonamide, sulfonate or sulfoximide groups for second harmonic generation.

5. FUNDING NUMBERS

C N00014-91-1338

6. AUTHOR(S)

Jody E. Beecher, Tony Durst, Jean M.J. Fréchet*, Adelheid Godt, Amy Pangborn, Douglas R. Robello, Craig S. Willand, David J. Williams

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Cornell University
Dept. of Chemistry, Baker Laboratory
Ithaca, New York 14853-1301

8. PERFORMING ORGANIZATION REPORT NUMBER

C N00014-91-1338

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale, its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The search for suitable NLO materials that are stable at elevated temperatures and that can be used for blue light generation requires that novel chromophores that can be incorporated into crosslinked polymers be developed. Several new tolane as well as stilbene chromophores with functionalized electron rich donor ends and electron-poor sulfonamide, sulfonate or sulfoximide ends have been prepared. These new chromophores have been evaluated for their transparency below 400 nm, and their molecular second-order hyperpolarizability has been measured by the EFISH method that provides $\mu\beta$values. The results of these measurements indicate that several of these new chromophores are capable of meeting the requirements for frequency doubling of a diode laser operating at 820nm. The chemistry of these new NLO chromophores allows their easy functionalization for incorporation of independently polymerizable groups at the donor and the acceptor ends of the molecules.

14. SUBJECT TERMS

NON-LINEAR OPTICS, NLO CHROMOPHORES, FREQUENCY DOUBLING, DIODE LASER, EFISH MEASUREMENTS SULFONATES, SUFONAMIDES, SULFOXIMIDE.

15. NUMBER OF PAGES 9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

OFFICE OF NAVAL RESEARCH

Grant # N00014-91-1338

R&T Code 413t003

Technical Report # 13

New chromophores containing sulfonamide, sulfonate or sulfoximide groups for second harmonic generation.

by Jody E. Beecher, Tony Durst, Jean M.J. Fréchet*, Adelheid Godt, Amy Pangborn
Douglas R. Robello, Craig S. Willand, David J. Williams

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

May 12, 1993

New Chromophores Containing Sulfonamide, Sulfonate, or Sulfoximide Groups for Second Harmonic Generation

Jody E. Beecher, Tony Durst, Jean M. J. Fréchet, Adelheid Godt, Amy Pangborn*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Douglas R. Robello, Craig S. Willand, David J. Williams

Electronic Systems Division, Eastman Kodak Company, Rochester, New York 14650

Introduction

Blue light generation for use in optical storage, printing, and other integrated optical applications has become a topic of intense research. Due to the lack of efficient lasers in this spectral region, the popular method of generating blue light involves frequency doubling of near infrared (800-850 nm) diode laser light using nonlinear optical (NLO) materials. Both organic and inorganic NLO compounds have been studied to date, but neither class has yet emerged as the material of choice. Efficient blue light generation requires that materials display not only a large nonlinear response, but also optical transparency at both the laser and blue light wavelength, i.e. colorless materials. This is particularly demanding on organic materials. Many electron-donor and electron-acceptor substituted π systems, including substituted benzenes, stilbenes, azobenzenes, and diphenylacetylenes (tolanes), are known to display large NLO responses. However, while conjugated π-systems with common acceptor substituents such as NO_2, CN or COR have large molecular hyperpolarizabilities, they suffer from low optical transparency in the region of blue light due to a low lying charge-transfer (CT) absorption.[1,2] The sulfone group was recently introduced as another acceptor substituent.[3,4] Donor-acceptor-substituted benzenes, styrenes, and tolanes with sulfone as the acceptor substituent show a remarkable molecular nonlinearity combined with a charge-transfer absorption band at relatively short wavelength.[3-6] Therefore, it seemed worthwhile to investigate the effect of the sulfonamide, sulfonate ester, and sulfoximide as acceptor groups on NLO properties. One example for sulfonamide as an acceptor for an NLO molecule is known, but no values for $\mu\beta$ have been published.[7] In addition to the expected low wavelength CT absorption, the multifunctional nature of these acceptor groups offers an easy way to derivatize them in order to develop crosslinkable polymers as NLO materials. In this paper we report on the synthesis and results of electric-field-induced second-harmonic generation (EFISH) measurements of such substituted tolanes and stilbenes.

Results and Discussion

Synthesis

The tolanes **5-7** (Scheme 1) were synthesized from appropriately substituted aryl halides using the methods developed by *Hagihara*[8] and *Negishi*.[9] In the first step, the synthesis of the arylacetylenes **3**, **4a** and **4b**, was achieved by reaction of the aryl iodides **1**, **2a**, or **2b** either with trimethylsilylacetylene in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI followed by desilylation,[8] or with ethynylzinc chloride under $Pd(PPh_3)_4$-catalysis.[9] The arylacetylenes **3**, **4a** and **4b** were then converted into the corresponding zinc chloride salts and coupled with aryl halides in the presence of catalytic amounts of $Pd(PPh_3)_4$[9] to give the tolanes **5-7** in overall yields of 40-50%.

Stilbenes **10a-d** (Scheme 2) were prepared using the *Heck* reaction.[10] The acceptor substituted arylbromides **8a-d** were coupled with *t*-BOC-styrene[11] in the presence of triethylamine and catalytic amounts of palladium diacetate and tri-o-tolylphosphine. The product, a mixture of the stilbenes **9a-d** and the corresponding *t*-BOC-substituted stilbenes, was treated with sodium methoxide affording stilbenes **9a-d** which were then alkylated to give stilbenes **10a-d** in 30-60% overall yields.

Spectroscopic and Nonlinear Optical Properties

The UV-vis spectroscopic and nonlinear optical properties of tolanes **5-7** and stilbenes **10** are summarized in Table 1. The UV-vis spectra of compounds **5-7** and **10** in $CHCl_3$, each show an intense low-energy absorption band which is rather narrow (ca. 55 nm half-height width). This band is assigned to an intramolecular CT transition. The wavelengths of the CT absorption bands are comparable with those reported for a 4-alkoxy-4'-sulfonyl-substituted stilbene (λ_{max} = 335 nm in $CHCl_3$)[4] or tolane (λ_{max} = 310 nm in dioxane).[5] It should be noted that the λ_{max} of the tolanes **5-7** determined in dioxane is 4-6 nm lower than λ_{max} determined in $CHCl_3$. As expected,[12] the CT-bands of the tolanes are blue-shifted significantly relative to the correspondingly substituted stilbenes. A comparison within the same π-system of the three different acceptor groups used, shows that the sulfonates usually absorb at longer wavelengths than the sulfonamides. The choice of N-substitution on the sulfonamide group has a small effect on λ_{max} as revealed by a comparison of stilbenes **10b** and **c**. The absorption of sulfoximide **10d** is similar to those of sulfonamides **10b**, **c** and sulfonate **10a**. Exchanging the methoxy-substituent for a methylthio-substituent[5,6,13] causes a red shift of the absorption by about 10 nm.

For electric-field poled materials, the macroscopic nonlinear optical response is directly related to the product of the molecular second-order hyperpolarizability (β), and the ground state dipole moment (μ). The values for $\mu\beta$ of the substituted tolanes and stilbenes (determined by the EFISH method[3]) are listed in Table 1. The largest values for a specific π-system, tolane or stilbene, are achieved with the sulfonate ester group. Changing from a sulfonate ester to a sulfoximide and further to a sulfonamide results in a decrease in $\mu\beta$. The values for $\mu\beta$ of the tolanes are always lower[5,12] than those of the corresponding stilbenes. Neither the exchange of a methoxy substituent for a methylthio substituent, nor the change of the N-substituent of the sulfonamide group have a profound effect on $\mu\beta$.

Although some of our data support the well known trade-off between $\mu\beta$ and λ_{max}, they also display remarkable deviations from this correlation. Stilbenes **10a** and **c** have the same λ_{max}, but they have very different values of $\mu\beta$. The same is true for tolanes **5a** and **6b**. In addition, the CT absorption band of tolane **6a** lies at 10 nm longer wavelengths than that of the tolane **5a** but the values of $\mu\beta$ are approximately the same. For the generation of blue light, the combination of a methoxy and sulfonate ester group, as in **10a**, appears to be the best of those studied in this paper: within one π-system, this combination leads to the highest $\mu\beta$ while maintaining a low λ_{max}. For comparison purposes 4-(6-hydroxyhexyloxy)-4'-(methylsulfonyl)stilbene was prepared by adaptation of literature procedures[3,4] and the value of $\mu\beta$ ($\mu\beta = 97 \cdot 10^{-48}$ esu; $\lambda_{max} = 335$ nm) determined using the same EFISH measurements. Clearly, the nonlinearity of sulfonate ester **10a** is superior to that of the 4-alkoxy-4'-sulfonylstilbene, confirming the validity of our approach to novel functional chromophores for NLO applications.

Acknowledgements. Financial support of this research by the Office of Naval Research and by the Eastman Kodak Company (Cornell Polymer Outreach Program) is acknowledged with thanks.

Table 1: Spectroscopic and nonlinear optical properties of the tolanes **5-7** and stilbenes **10** in $CHCl_3$. λ_{EFISH} = 1907 nm.

	Donor	Acceptor	λ_{max}(log ε) (nm)	μβ (10^{-48} esu)
5a	MeO	SO_3Ph	321 (4.473)	89
5b	MeO	SO_2NBu_2	312 (4.504)	49
6a	MeS	SO_3Ph	331 (4.518)	95
6b	MeS	SO_2NBu_2	324 (4.556)	59
7	Me_2N	SO_2NBu_2	359 (4.534)	--
10a	EtO	SO_3Ph	340 (4.420)	160
10b	EtO	SO_2NBu_2	335 (4.512)	100
10c	EtO	SO_2NPh_2	340 (4.526)	95
10d	PrO	S(O)(NH)Me	338 (4.550)	130

References and Notes

[1] D. J. Williams, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690 and references therein.

[2] L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631.

[3] A. Ulman, C. S. Willand, W. Köhler, D. R. Robello, D. J. Williams, L. Handley, *J. Am. Chem. Soc.* **1990**, *112*, 7083.

[4] G. L. J. A. Rikken, C. J. E. Seppen, S. Nijhuis, E. W. Meijer, *Appl. Phys. Lett.* **1991**, *58*, 435.

[5] D. M. Burland, R. D. Miller, O. Reiser, R. J.Twieg, C. A. Walsh, *J. Appl. Phys.* **1992**, *71*, 410.

[6] A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L.-T. Cheng, J. Perry, W. *J. Am. Chem. Soc.* **1991**, *113*, 7658.

[7] S. Allen, D. J. Bone, N. Carter, T. G. Ryan, R. B. Sampson, D. P. Devonald, M. G. Hutchings, in *Organic Materials for Nonlinear Optics II* (Eds: R. A. Hann, D. R. Bloor), Soc. Chem. **1991**; p. 235.

[8] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis*, **1980**, 627.

[9] A. O. King, E. Negishi, *J Org. Chem.* **1978**, *43*, 358.

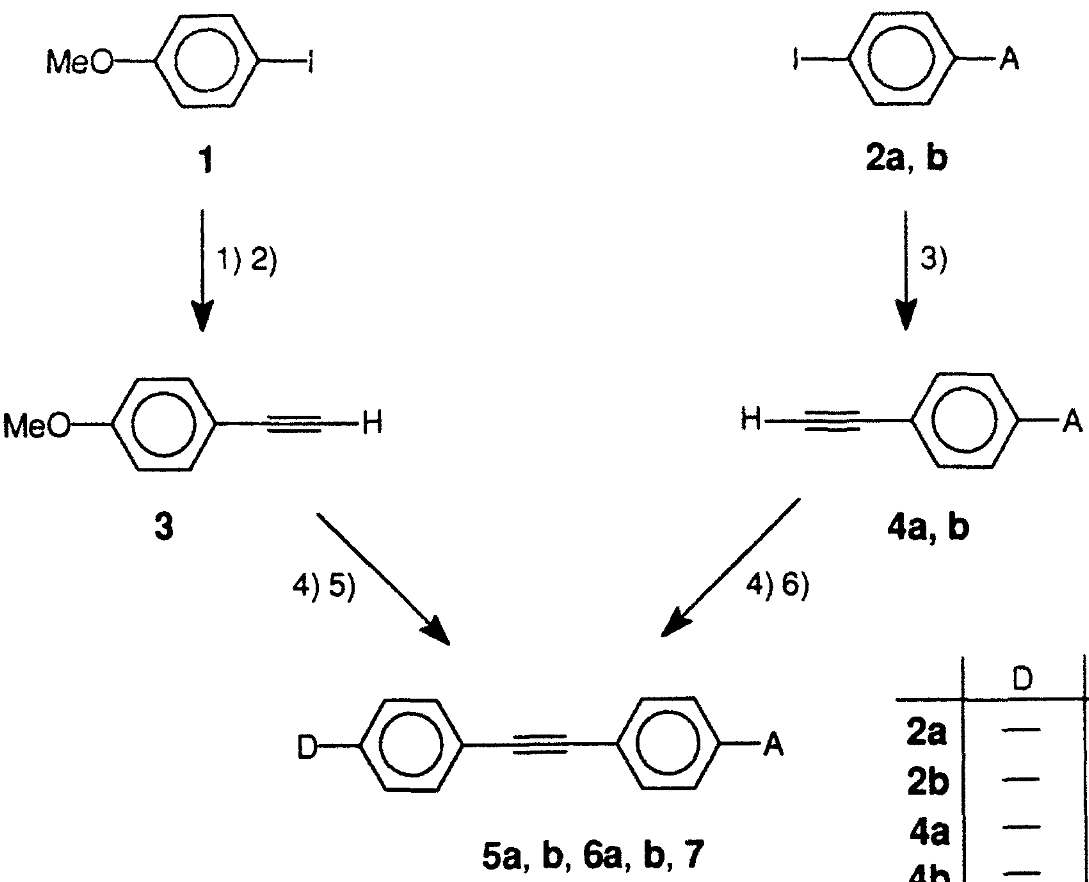
[10] R. F. Heck, *J. Org. Chem. Soc.* **1982**, *43*, 2454.

[11] J. M. J. Fréchet, E. Eichler, C. G. Willson, H. Ito, *Polymer.* **1983**, *24*, 995.

[12] L.-T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, *J. Phys. Chem.* **1991**, *95*, 10643.

[13] M. Barzoukas, A. Fort, G. Klein, A. Boeglin, C. Serbutoviez, L. Oswald, J. F. Nicoud, *Chemical Physics* **1991**, *153*, 457.

SCHEME 1



	D	A
2a	—	SO_3Ph
2b	—	SO_2NBu_2
4a	—	SO_3Ph
4b	—	SO_2NBu_2
5a	MeO	SO_3Ph
5b	MeO	SO_2NBu_2
6a	MeS	SO_3Ph
6b	MeS	SO_2NBu_2
7	Me_2N	SO_2NBu_2

1) $HCCSiMe_3$ / $Pd(PPh_3)_2Cl_2$ / CuI / Et_2NH / rt;

2) NaOH / MeOH / rt;

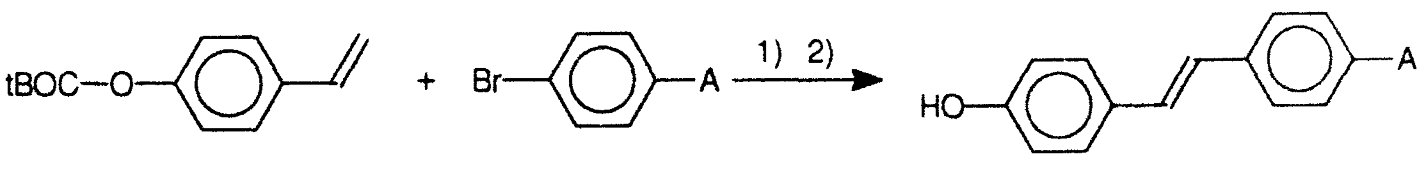
3) HCCZnCl / $Pd(PPh_3)_4$ / THF / rt;

4) a) *n*-BuLi / THF / -78 °C; b) $ZnCl_2$ / -78 °C; c) $Pd(PPh_3)_4$ / 0 °C;

5) p-I-C_6H_4-SO_3Ph / rt or p-Br-C_6H_4-SO_2NBu_2 / reflux;

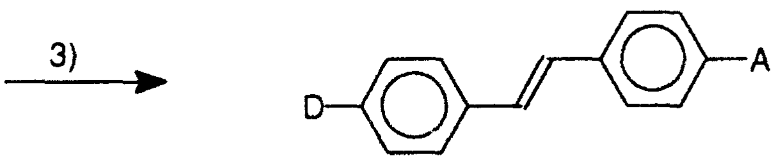
6) p-MeS-C_6H_4-Br / reflux or p-Me_2N-C_6H_4-I / rt;

SCHEME 2



8

9



10

8,9,10	D	A
a	EtO	SO_3Ph
b	EtO	SO_2NBu_2
c	EtO	SO_2NPh_2
d	PrO	SO(NH)Me

1) $Pd(OAc)_2$ / P(o-tolyl)$_3$ / Et_3N / MeCN / rt;

2) NaOMe / MeOH / rt;

3) K_2CO_3 / RBr / DMF / rt;